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Research on 5*f* electron systems: Surprises at the end of the periodic table

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October 08

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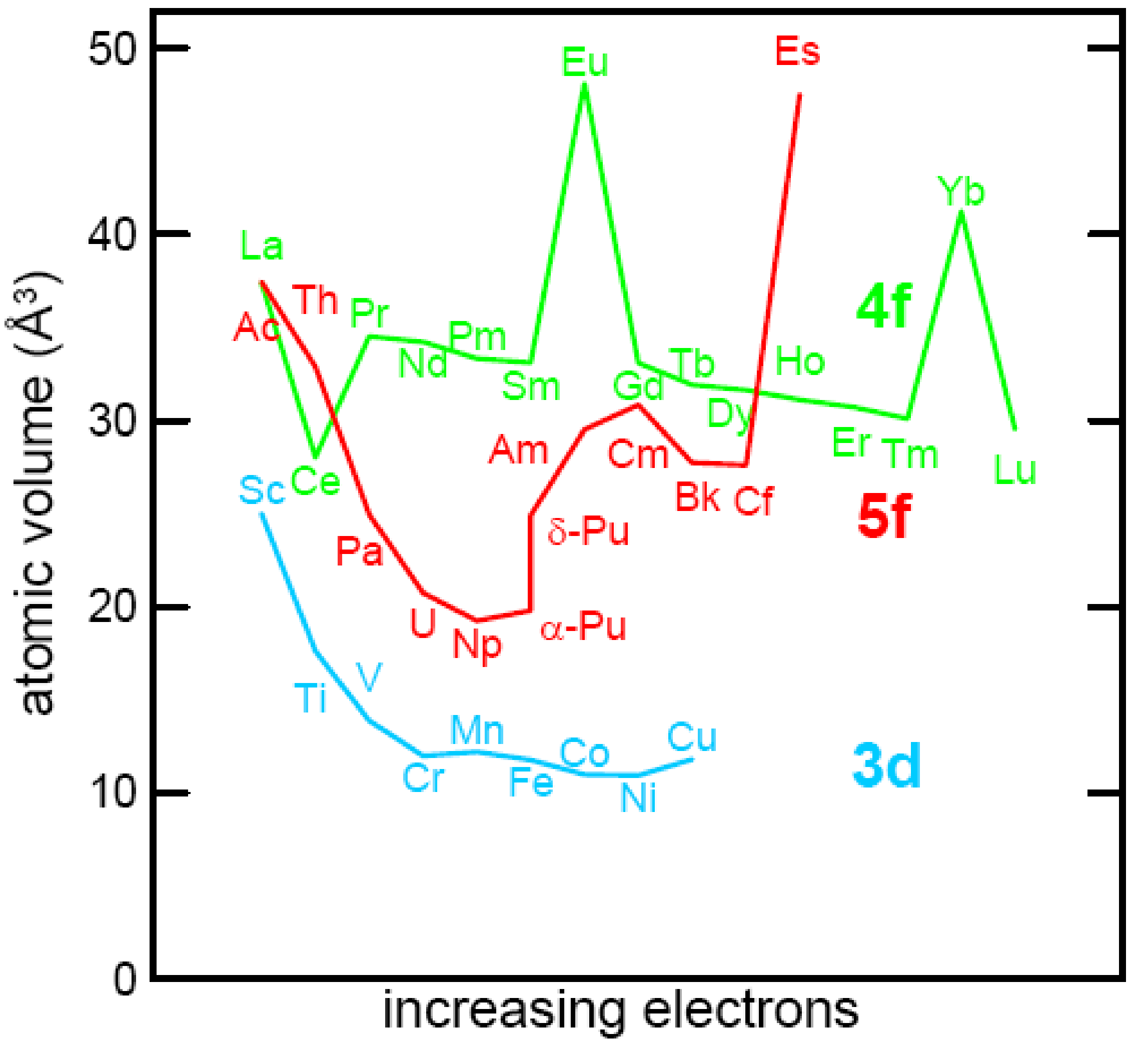
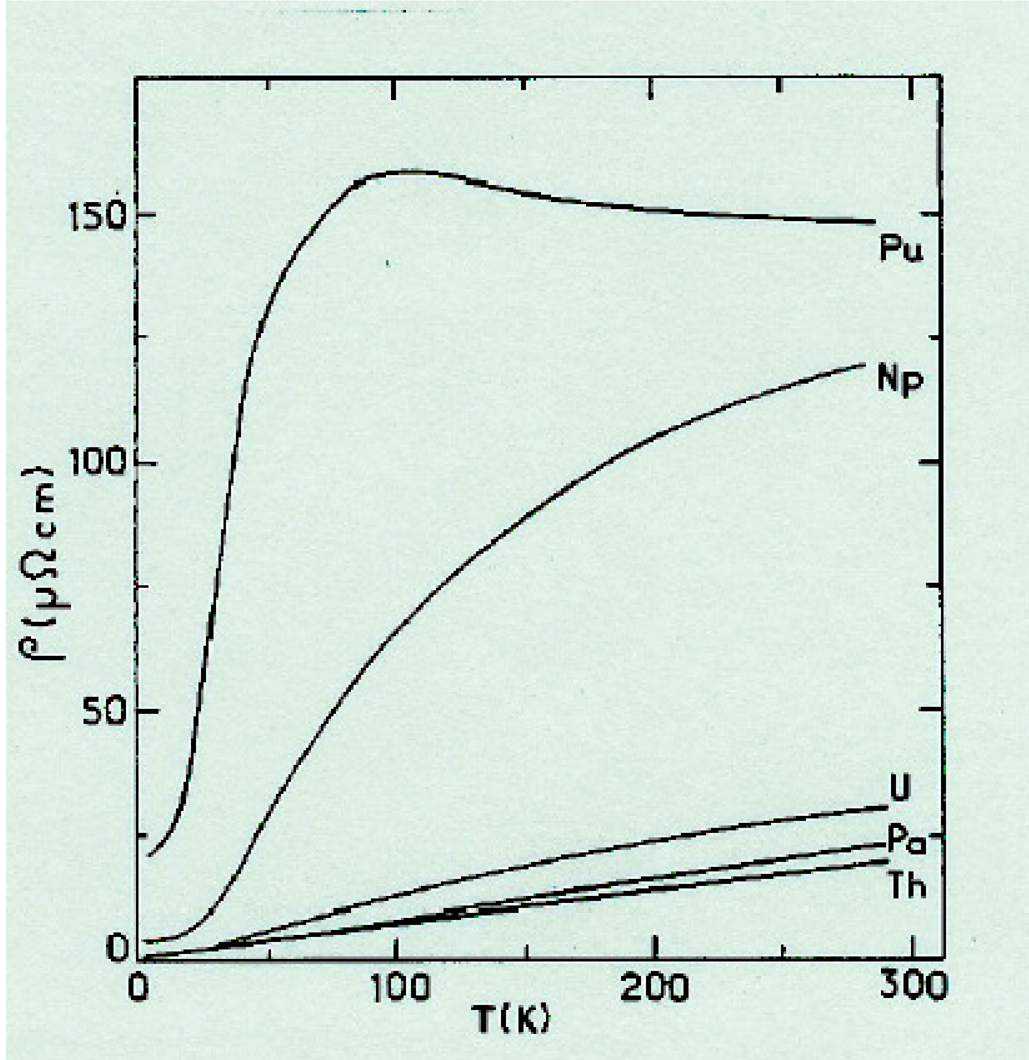


Elemental volumes

Electrical resistivity

- Note unusual resistivity in Pu
  – suggests a Kondo effect.

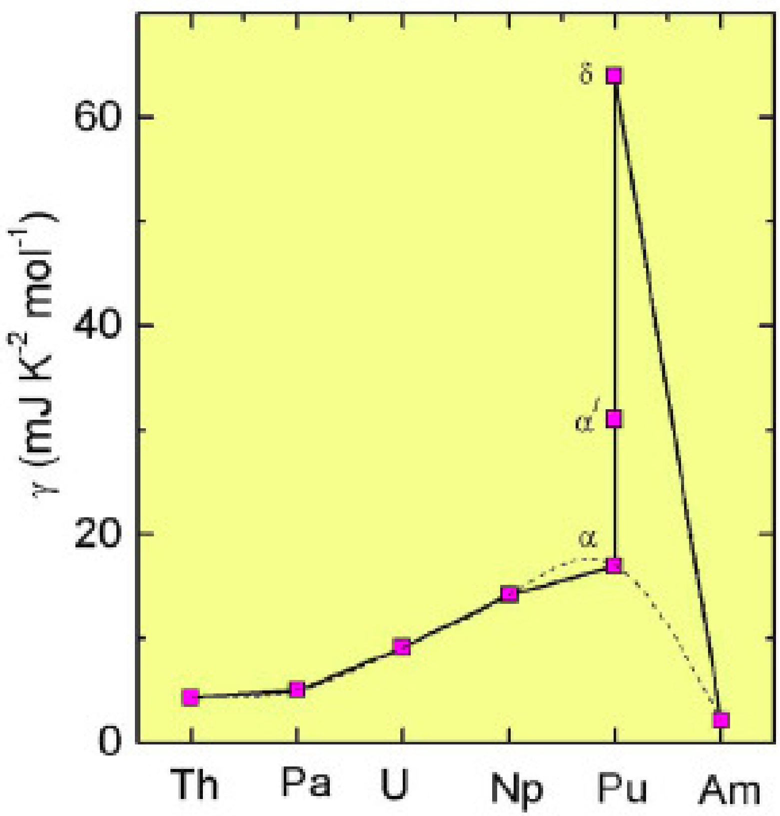


•Taken from Fournier & Troc (1985)

•p. 45 Fig. 2

Sommerfeld coefficients of the elements

- The early actinides Th – Np show specific heat γ coefficients consistent with broad *d*- or *f*-band materials
- In Pu for the first time strong correlation effects are clearly present
- With the localization at Am the γ falls to almost zero.



J. C. Lashley *et al.* PRB 72 054416 (2005)

The elements: Pa to Bk

- Th (*bcc*) and Pa (*bct*) are considered tetravalent; low (< 5 mJ/mole/K^2) γ values. However, *bcc* structure is stabilized by ~ 0.5 5*f* state, and complex structure in Pa shows ~ 1.5 5*f* electrons. Such 5*f* states are lost on forming compounds.
- U, Np, and Pu have wide (but they narrow with additional electrons) bands and 5*f* states (3, 4, & 5), but they have NO ordered magnetism
- Am is the first localized element but with 6 5*f*'s the *j=5/2* shell is full (L=–S=3; J=0) and NO magnetism
- Cm, Bk are strongly magnetic; large moments and $5f^7$ and $5f^8$ states, respectively

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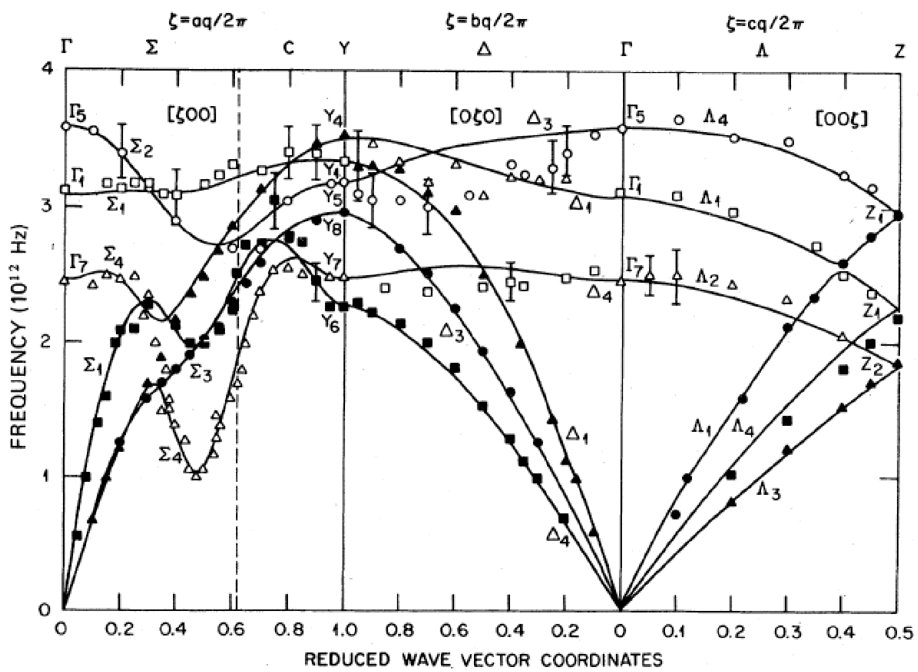
Electron-phonon coupling in alpha–U drives a charge-density wave

- **Orthorhombic Cmcm**
- **Anomalies had already been reported in elastic constants by Fisher *et al.*, in the 1960s.**
- **Phonon dispersion curves (here shown at RT) indicated nature of atomic displacements**
- **CDW condenses at 43 K**

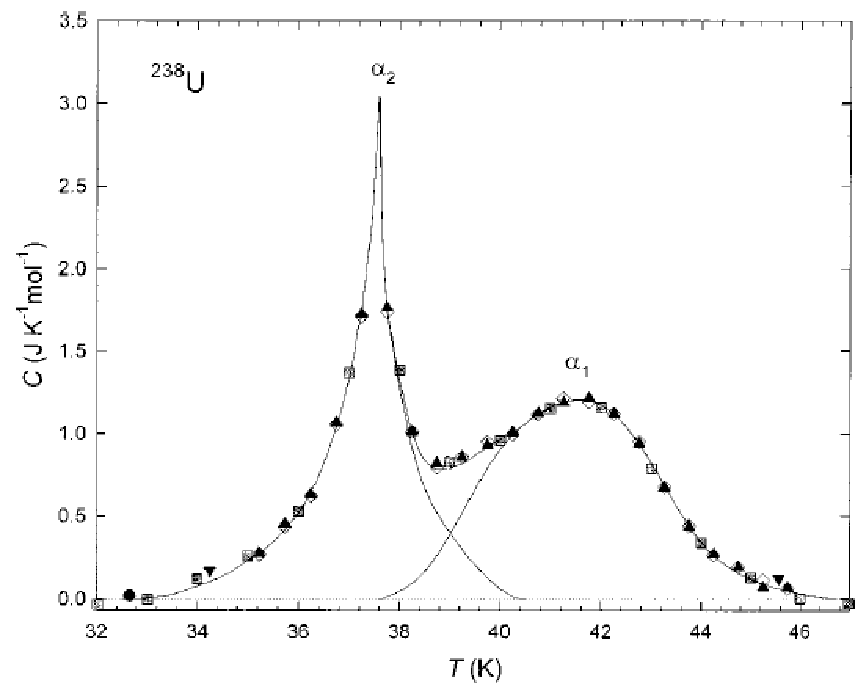


W. P. Crummett *et al.*, PRB <u>19</u> 6028 (1979)

Observation of CDW by specific heat

- **Specific heat, as measured in the 1960s, had already seen anomalies, but we show here some more recent work identifying the phase transitions as 2nd and 1st–order at 43 and 37.5 K, respectively.**

Excess specific heat



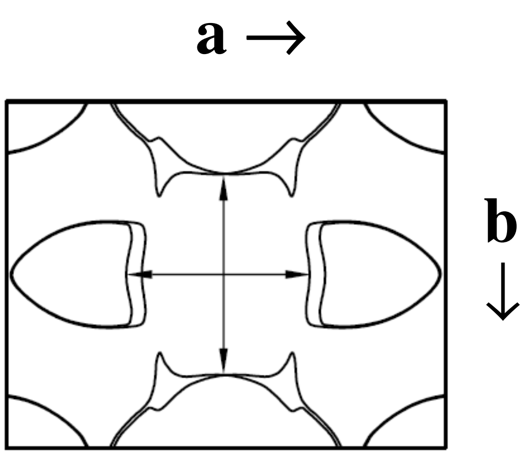
J. C. Lashley *et al.*, PRB 63 224510 (2001)

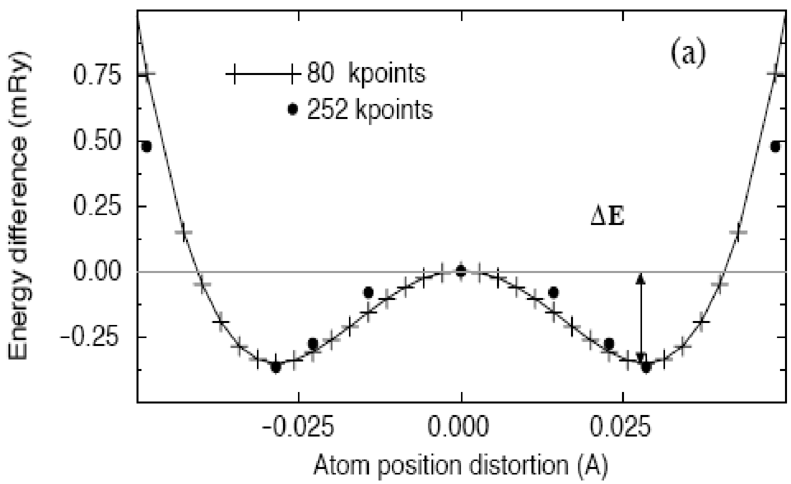
Theory & the CDW

- The strong nesting in α–U gives rise to the Kohn anomaly that condenses as a CDW or Peierls distortion

Adv. Physics 43 1-110 (1994)

- Fast *et al.*, also predicted that strong e-p coupling will even give rise to the phonon anomaly *above* the transition temperature
- This has now been observed



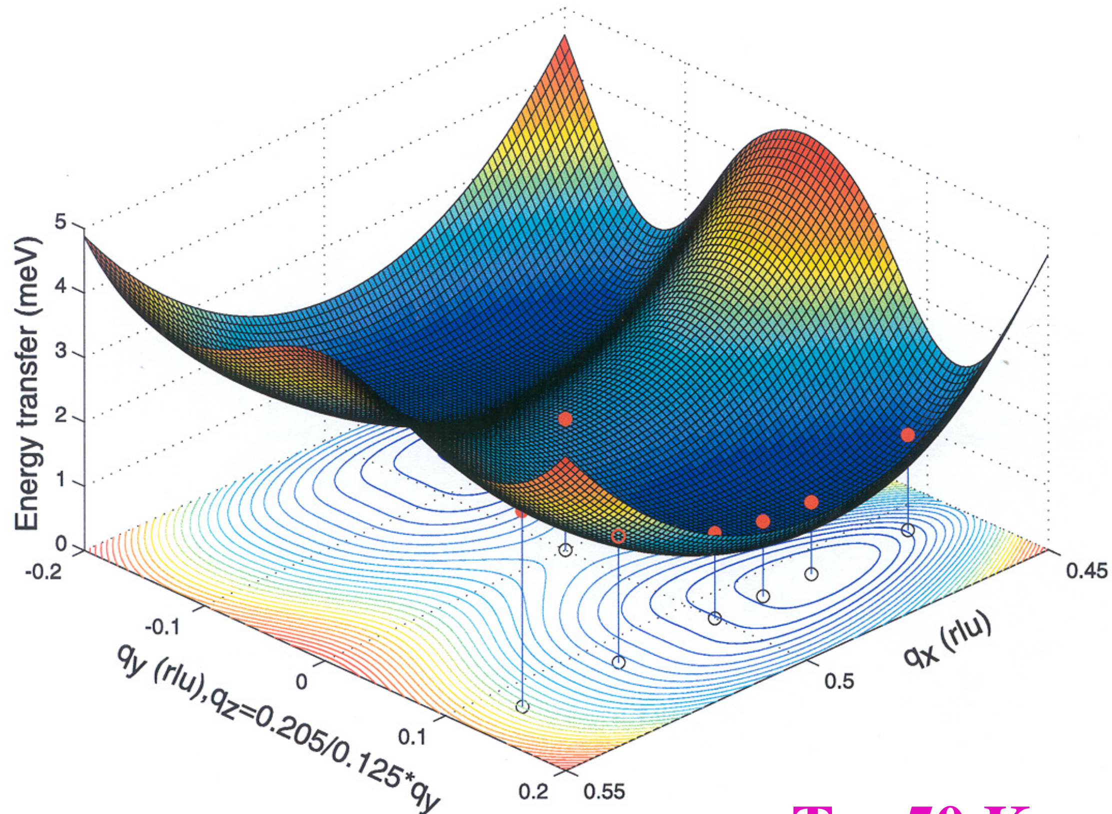


[100] (a) direction

L. Fast *et al.*, PRL 81 2978 (1998)

Characterization of the soft mode in alpha-U

**The position of the minimum in the phonon spectrum *above T_o* shows the importance of the electron-phonon interaction in driving the CDW.
Note that the minimum is *not* at $q_x = 1/2$**



T = 50 K

$T_0 + 7$ K

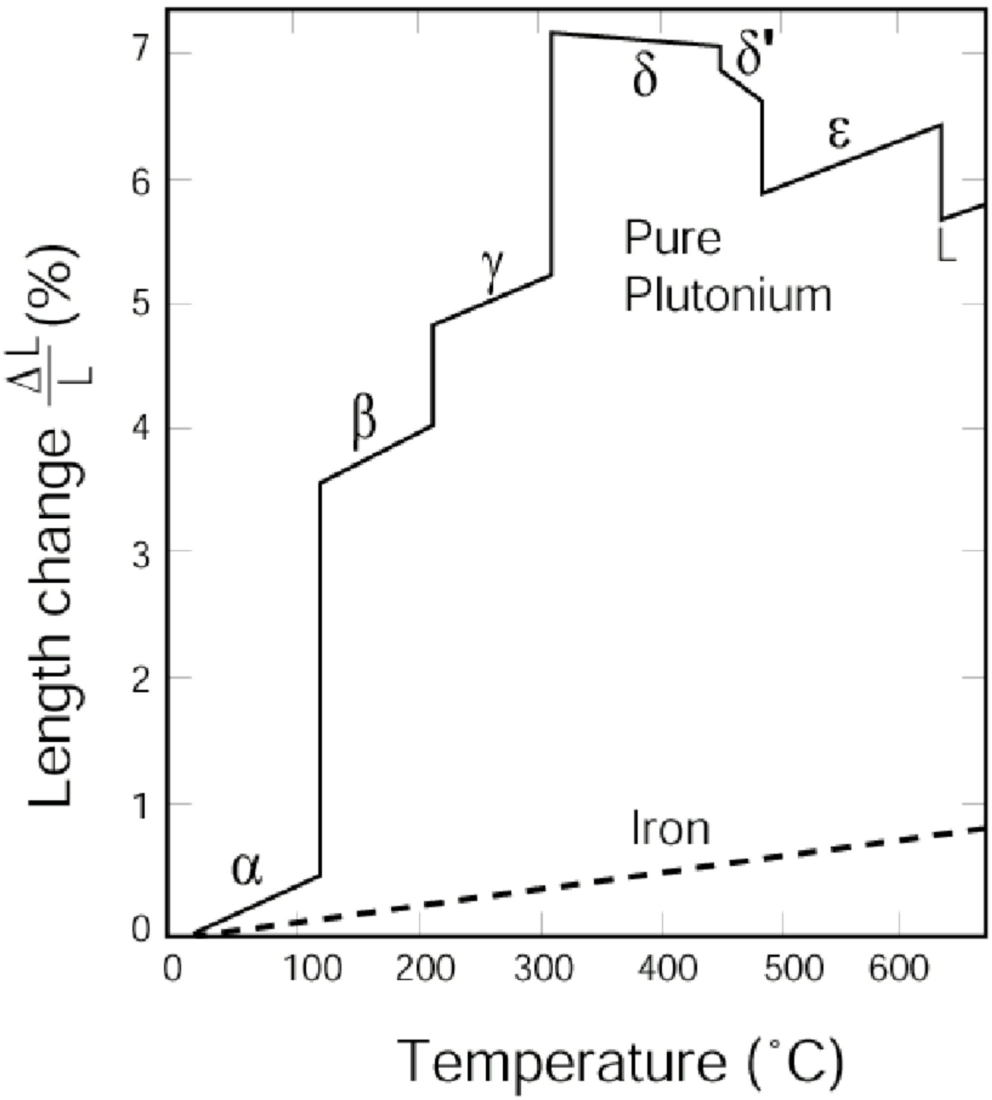
Experiments at ILL, J. C. Marmeggi *et al.*

Plutonium

The most complex element in the periodic table!

Thermal expansion in the 6 phases of Pu

Note the large change from α to δ



Susceptibility of Pu

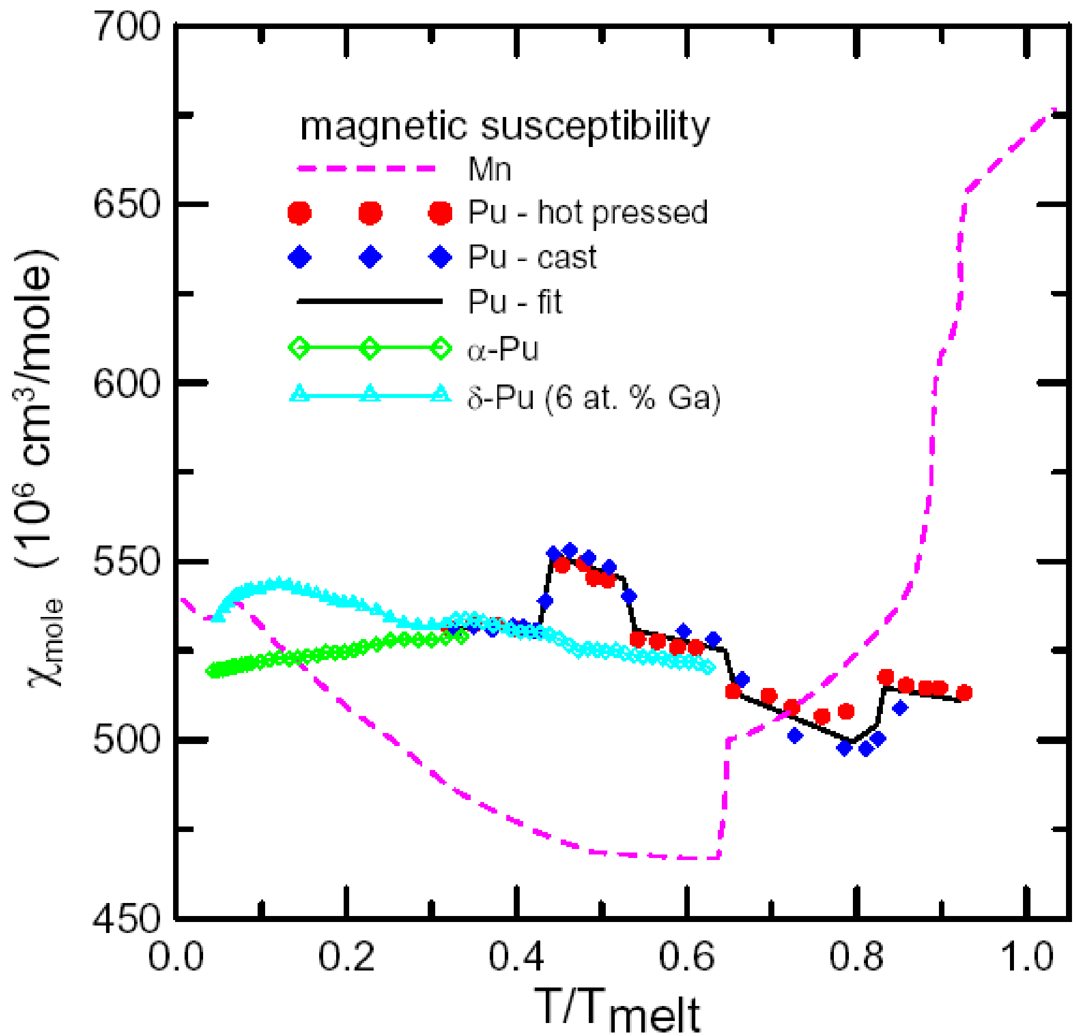
- Pu

$T_m = 913$ K

- Mn

$T_m = 1519$K

$T_N = 140$ K

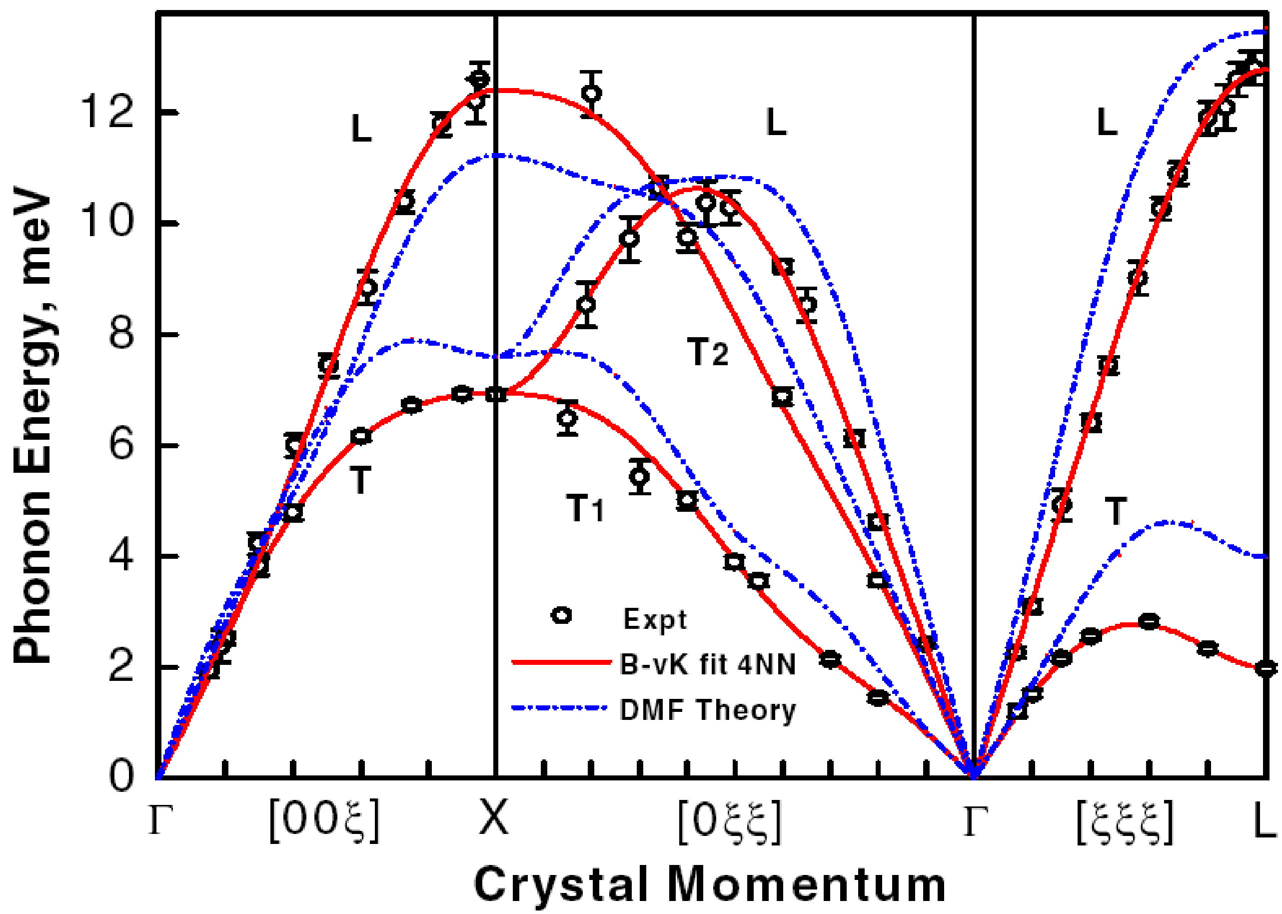


Magnetism in δ-Pu?

- There has never been much evidence for moments of any form in Pu, and the most recent experiments have left *no* doubt whatsoever. **Only theory predicted strong magnetism!**
- χ ρ γ (C/T)
- NMR Piskunov *et al.* PRB <u>71</u> 174401 (2005)
- NMR Curro & Morales MRS Proc. <u>802</u> 53 (2004)
- Neutron elastic & inelastic, Lashley *et al.* PRB <u>72</u> 054416 (2005)
- Muons, Heffner *et al.*, PRB <u>74</u> 094453 (2006)

Fluctuations on low-energy (a few meV) scale can be excluded, but *not* a large energy scale, e.g. ~ 100 meV

Phonons in δ–Pu(fcc)



- Theory, Dai & Kotliar in Science, 2003
- J. Wong *et al*, LLNL, Science, 2003;

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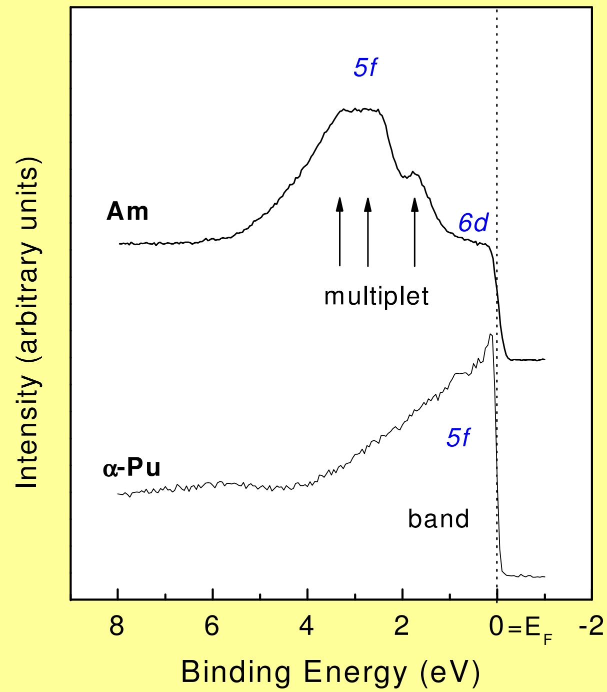
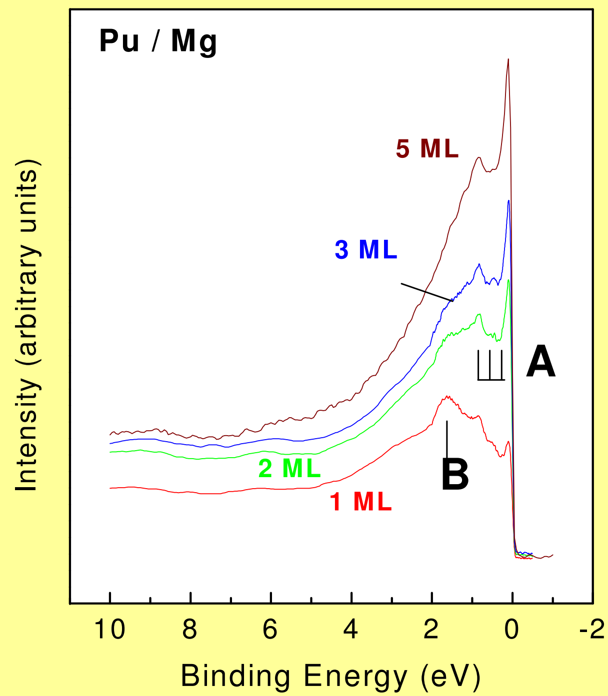
5f localization: Films and Bulk Systems

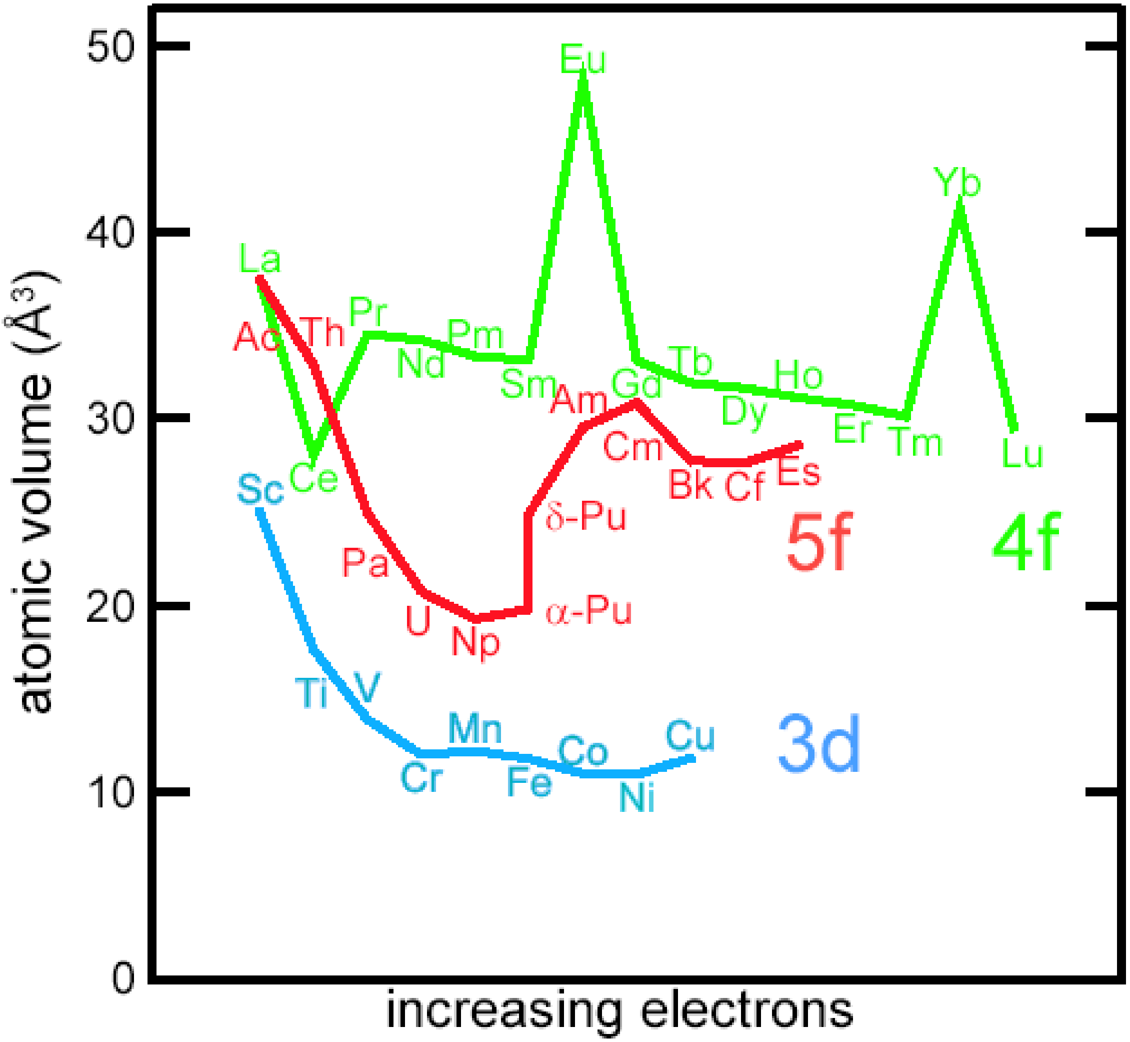




T. Gouder et al. **EPL 55** (2001), 705

Localization:
5f at higher BE
Multiplet structure

Band -> Intermediate Loc. (A) -> Full Loc. (B)



Elemental volumes

Americium

Am (Rn)$5f^7 6d^0 7s^2$: Am^{3+} $5f^6$

With its expanded volume one presumes that Am is localized. The γ is small (~ 5) and theory suggests that the $5f^{5/2}$ state is full with 6 $5f$ electrons and the $5f^{7/2}$ is empty.

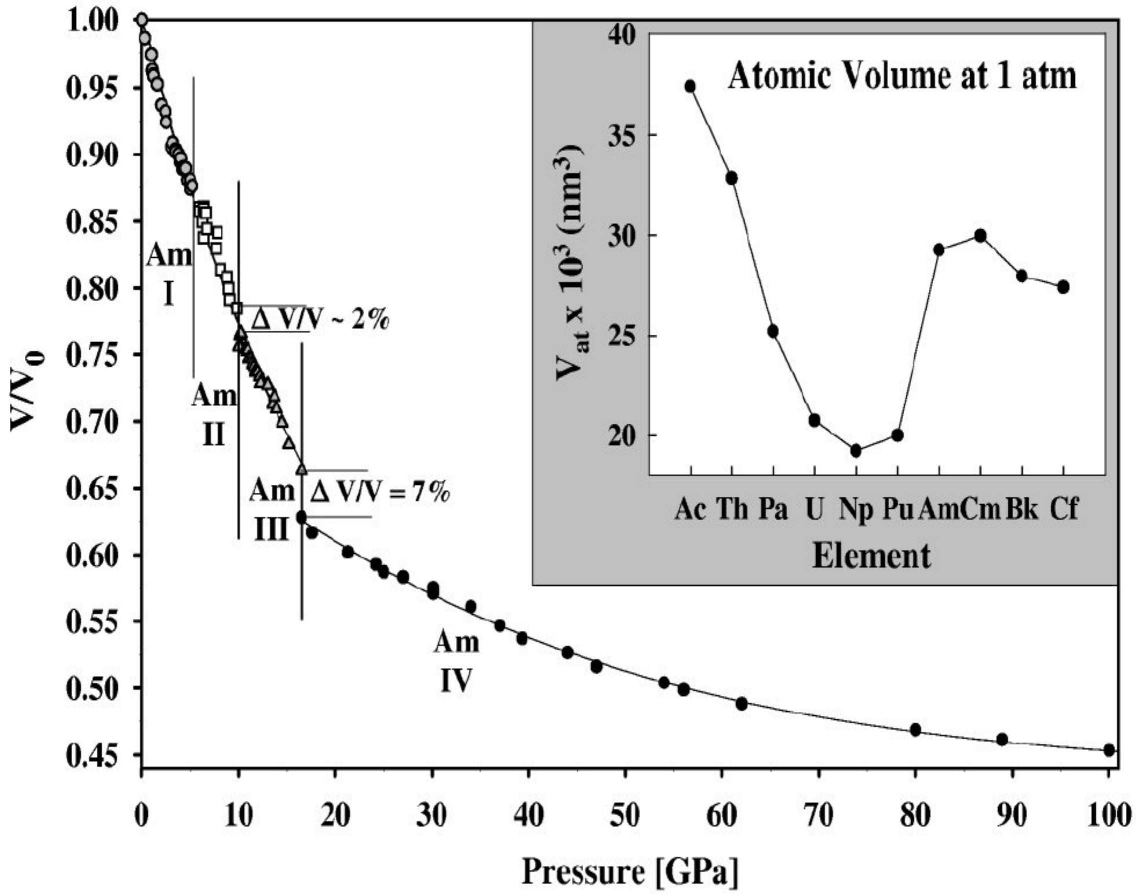
In RS coupling this gives L = 3 = –S; J =0

AmI – dhcp

AmII – fcc

AmIII
Fddd (ortho)
like γ–Pu

AmIV
Pnma (ortho)
like α-U



S. Heathman *et al.*, PRL 85 2961 (2001)
A.Lindbaum *et al.*, PRB 63 214101 (2003)

Americium: T_c vs p

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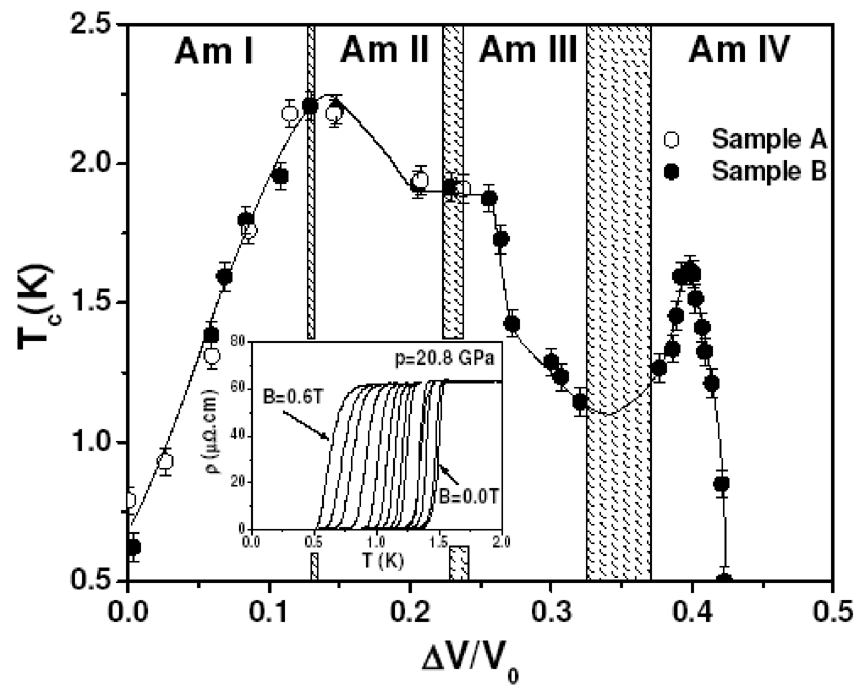
- Am s/c predicted (by Johannson) in 1975; confirmed in 1978

- Crucial question is what happens as pressure is increased and 5*f* states transform from *localized to itinerant* through a Mott transition

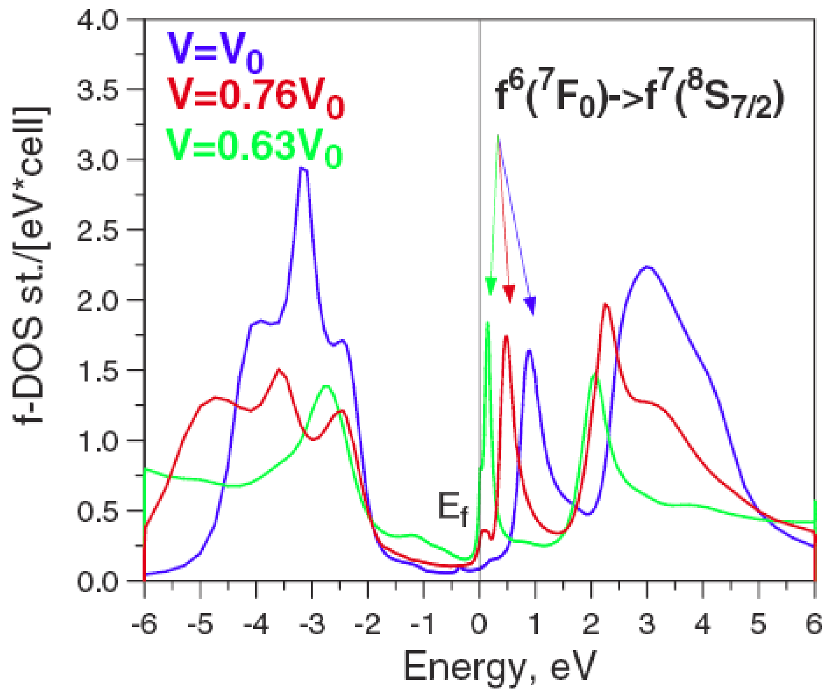


J-C Griveau *et al.* PRL <u>94</u> 097002 (2005)

Density of states as a function of atomic volume

Mott transition, AmIII to AmIV occurs at $V/V_0 \sim 0.65$

Mixing occurs with the f^7 state as this passes through E_F.



S. Y. Savrasov *et al.*, PRL 96 036404 (2006)

Curium: $5f^7 6d^1 7s^2$: Cm^{3+} $5f^7$

Trivalent state is very stable

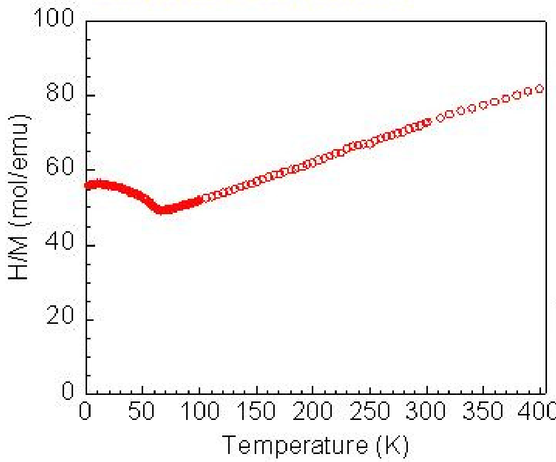
dhcp reported AF T_N = 64 K

AF structure not known

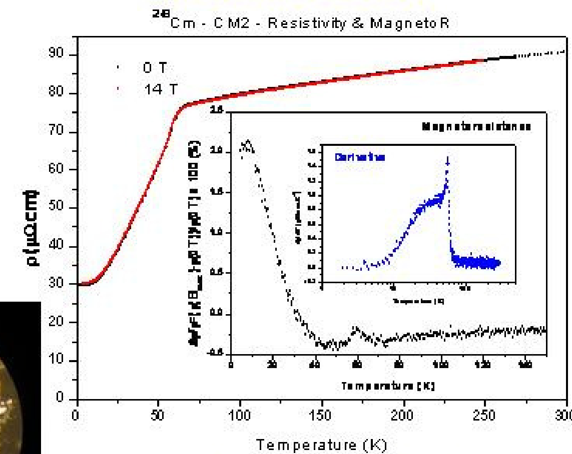
Effective moment = 7.6 μ_B

Magnetic and transport properties of ^{248}Cm metal

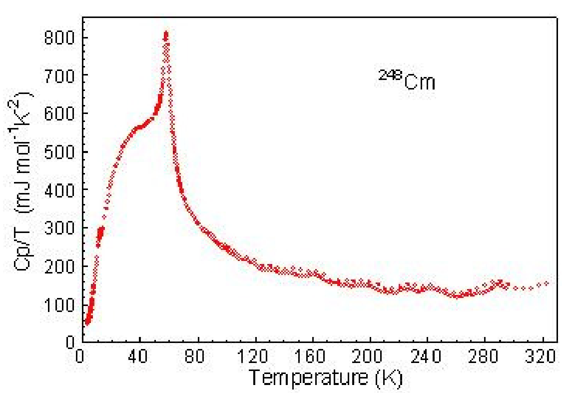
Magnetic susceptibility



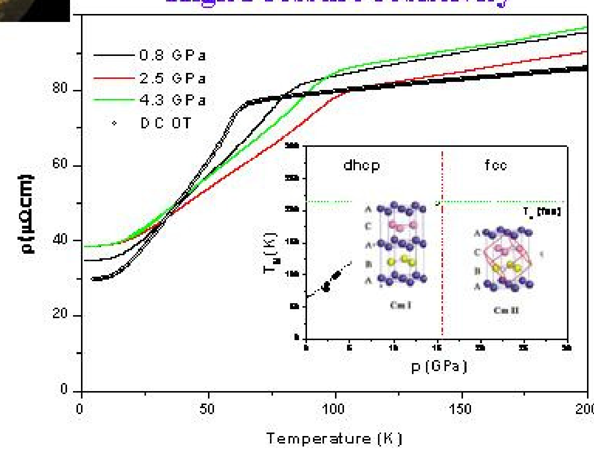
Electrical resistivity



Specific heat



High Pressure resistivity



Measurements at ITU, E. Colineau, J-P. Griveau, J. Rebizant, R. Caciuffo, and R. Haire (ORNL)

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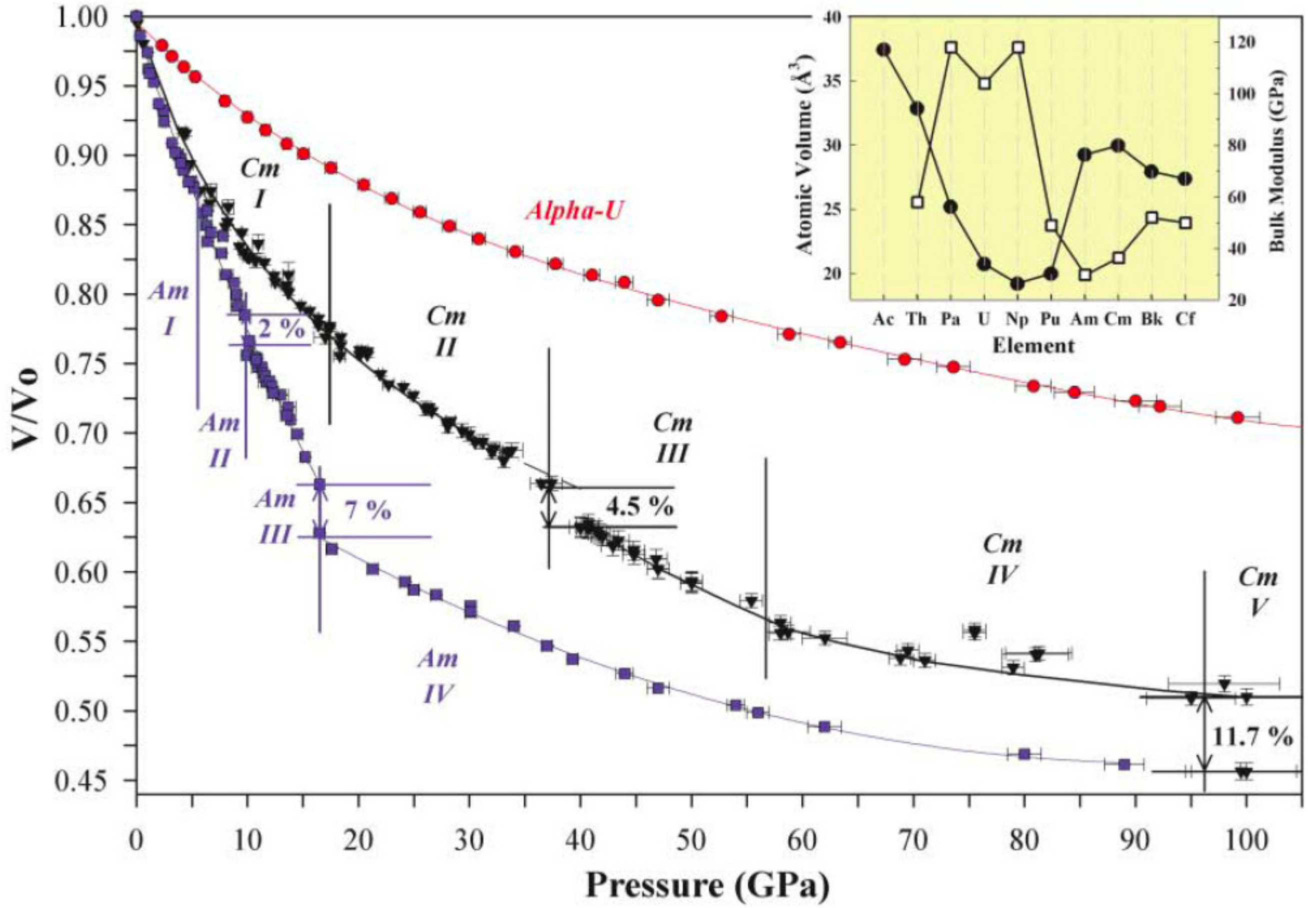
Curium has 5 phases to 100 GPa



S. Heathman *et al*, Science 309 110 (2005)

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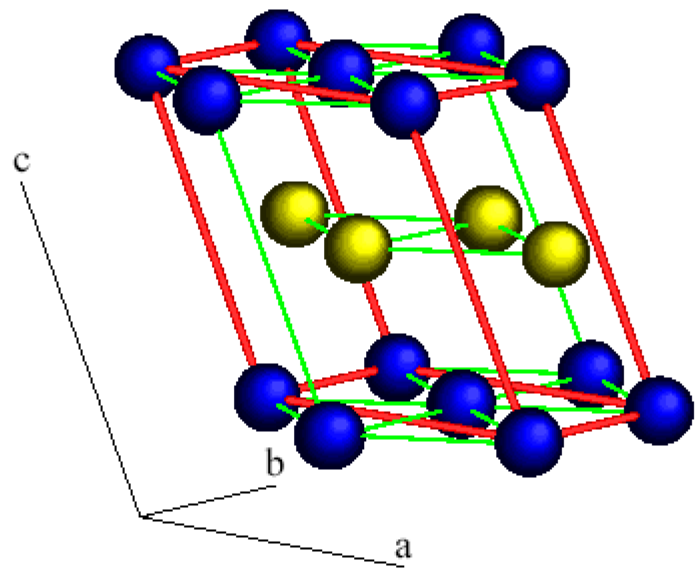
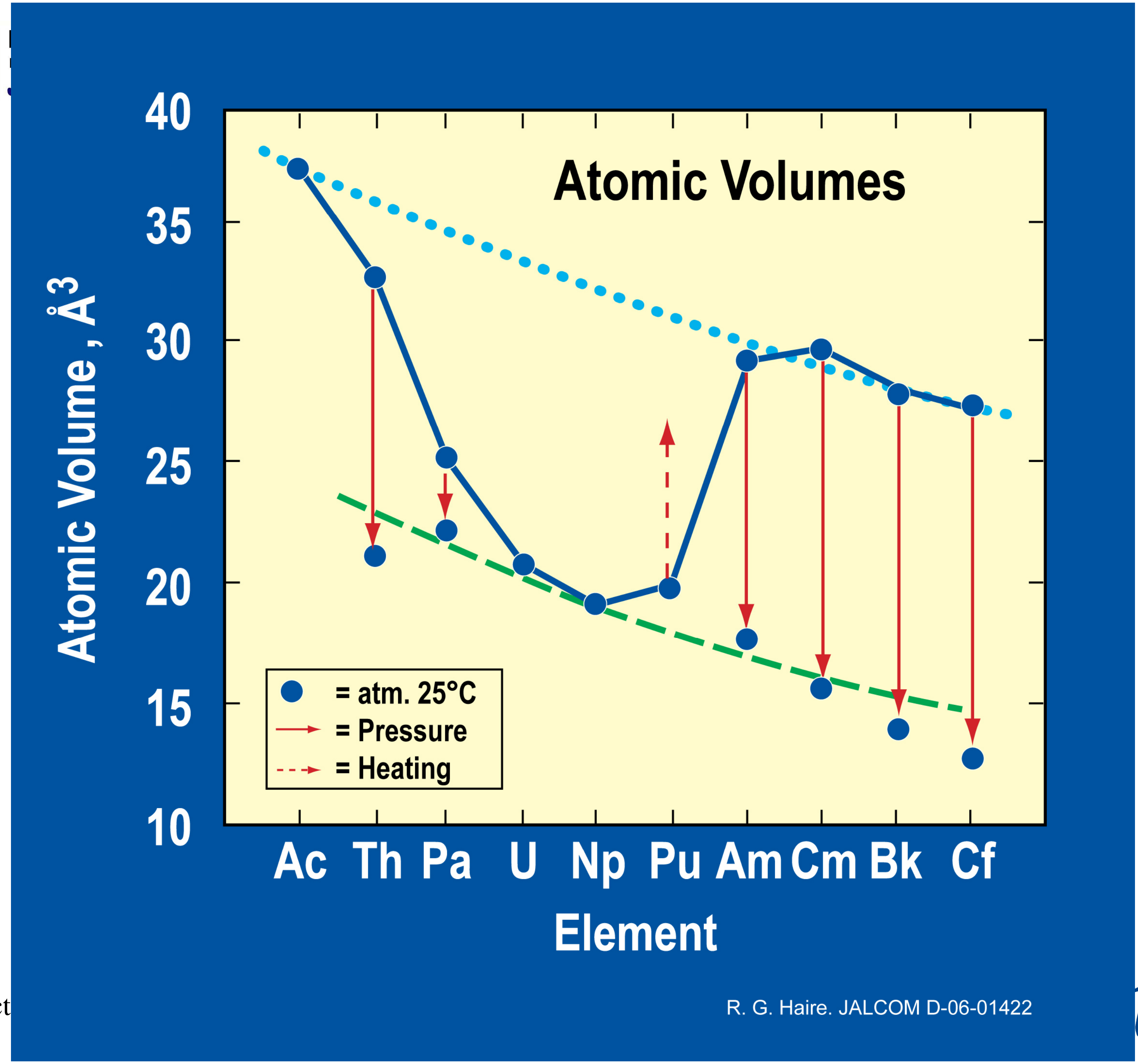
Cm III structure unique

- Cm III is stable between 37 - 56 GPa
- **Monoclinic structure C2/c; β = 116º**
- **Partial collapse of 4.5% from Cm II.**
- **Theory suggests that this structure is stabilized by antiferromagnetic exchange.**
- **In the CmIV phase (56 GPa and ~ 0.5 V_O) there is no moment and the 5*f* electrons are itinerant**
- **final 12% collapse into Cm V (same as Am IV)**



S. Heathman *et al*, Science 309 110 (2005)


Atomic Volumes
Atomic Volume , Å^3
40
35
30
25
20
15
10
= atm. 25°C
= Pressure
= Heating
Ac Th Pa U Np Pu Am Cm Bk Cf
Element
R. G. Haire. JALCOM D-06-01422

Acknowledgments for the elements

- **ANL:** Ed Fisher, Sam Bader, Mel Mueller
- **Grenoble:** Roland Currat, Jean-Claude Marmeggi, Tristan le Bihan
- **BNL:** John Axe, Doon Gibbs, Gerhard Grübel
- **ORNL:** Dick Haire, Harold Smith
- **LANL:** Angus Lawson, Jason Lashley, Rob McQueeney, John Wills, Bob Heffner
- **ITU:** Jean-Christoph Griveau, Steve Heathman
- **Rutgers:** Gabi Kotliar (theory)
- **Uppsala:** Rajeev Ahuja, Borje Johansson (theory)
- **LLNL**: Kevin Moore, Jim Tobin

Thin films of uranium: multilayers and epitaxial layers

The development of sputtering capability (at Oxford University, UK) has opened a number of new possibilities for uranium research, and perhaps later (at a closed Lab) of transuranics.

Production of multilayers:
U/Fe, U/Co, U/Ni, U/Gd: structural characterization
What is polarization of U 5*f* states?

Production of epitaxial layers:
Alpha-U grows well on Nb buffers
Characterization – is there a CDW?
Can other structures of uranium be made?

Multilayers containing uranium

Study of growth parameters given intermediate size of U (~21 Å^3) between *3d* (~12 Å^3) and 4*f* (~33 Å^3).

Roger Ward & Mike Wells (Oxford U) – fabrication & characterization

Angela Beesley & Mike Thomas (U. Liverpool) – Mössbauer effect

Ross Springell & Stan Zochowski (UC London) – magnetization and transport

Sean Langridge (ISIS, RAL) – PNR

Fabrice Wilhelm (ESRF) – XMCD

Simon Brown, Laurence Bouchenoire & Stuart Wilkins (ESRF) – X-ray magnetic resonant reflectivity (XMRR)

W. J. MoberlyChan, R. Gross, M. Butterfield & K. T. Moore (LLNL) TEM

W. G. Stirling (ESRF) & **G.H.Lander** (ITU) – secretaries & cheerleaders

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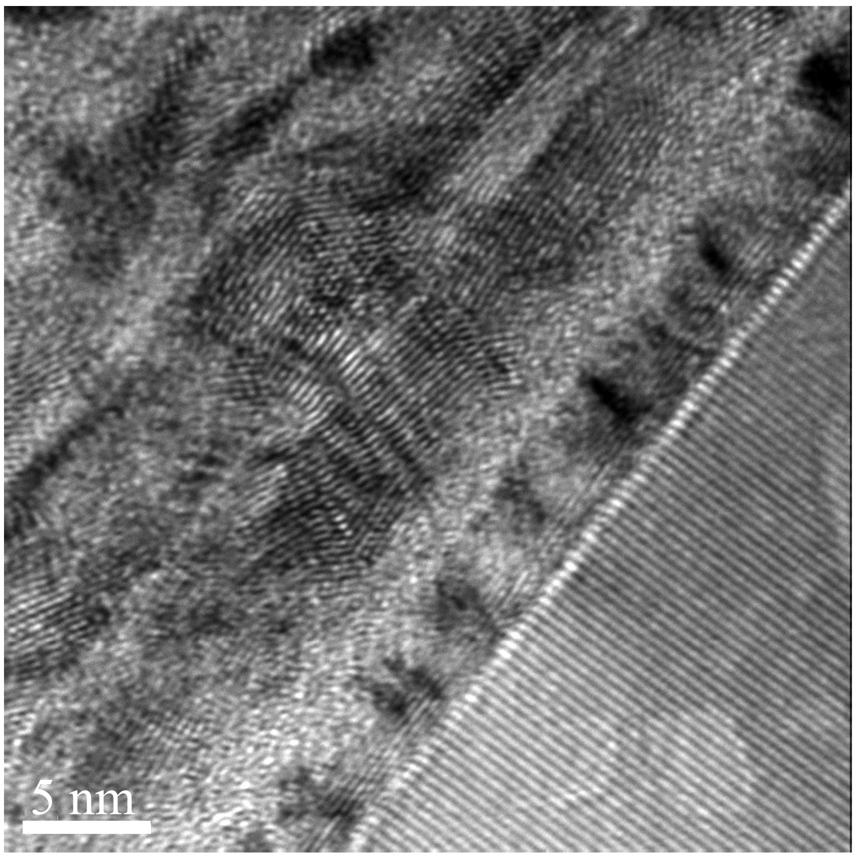
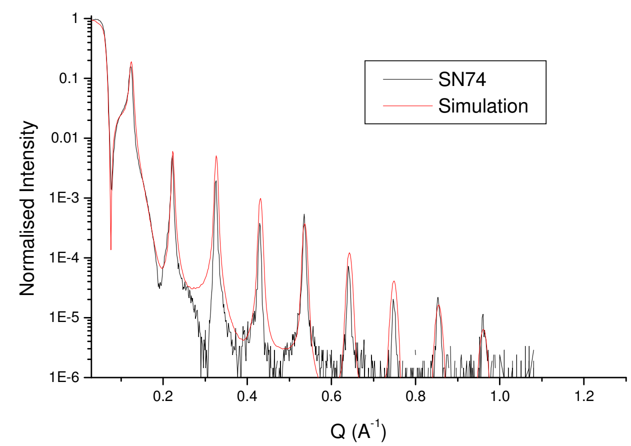
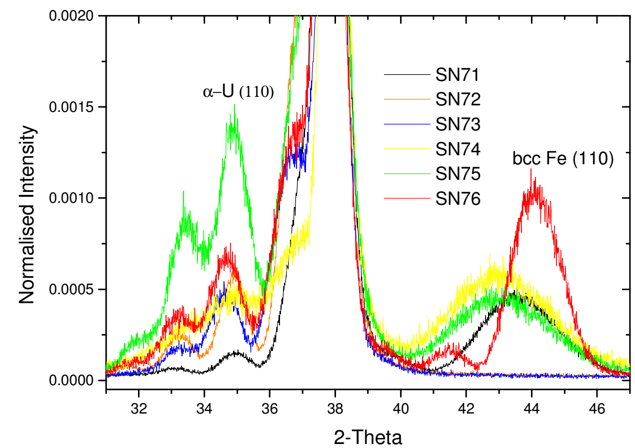
Characterization of multilayers by x-ray reflectivity, high-angle XRD and TEM

$[U_{30}/Fe_{30}]_{30}$







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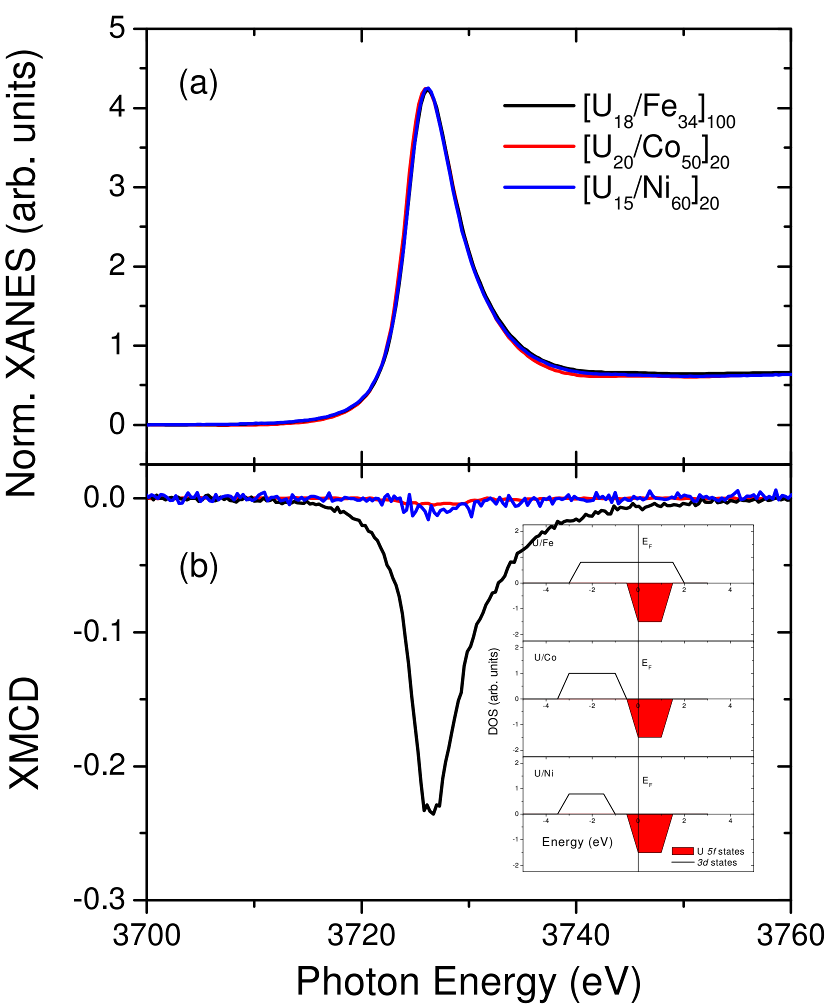
Characteristics of U/Transition-metal multilayers

Growth difficult. **TM** shows crystallinity and preferred orientation as expected. **U** is not strongly crystalline, but shows preference for **α–U** structure. Considerable roughness, becoming progressively worse for Co and Ni than for Fe.

Magnetic characterization:

SQUID and polarized neutrons see the behavior of the TM Element sensitive techniques such as x-ray circular dichroism (XMCD) and x-ray magnetic reflectivity (XRMR) are able to use the large enhancements at the U $M_{4,5}$ edges to probe the effect on the U 5*f* states.

Magnetic properties of U 5*f* states in U/TM multilayers

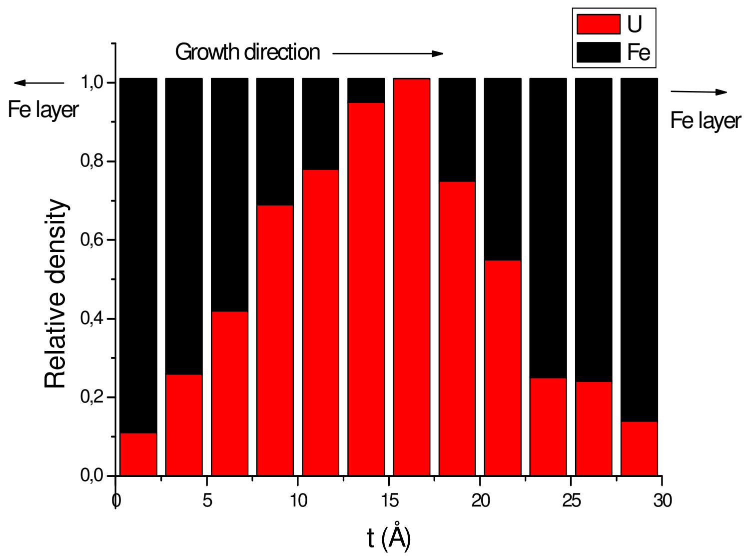


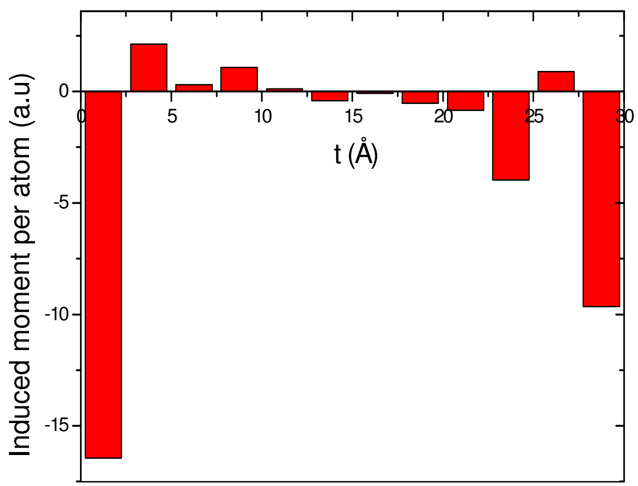
Strong U polarization is found *only* in U/Fe multilayers.

We assume this is because the 5*f* states are at E_F and the 3*d* states move progressively lower in energy from Fe → Co →Ni, thus decreasing the overlap with the 5*f* states and reducing the induced moment.

Springell *et al*. PRB 77 064423 (2008)

Distribution of moment in U layers





Element selective measurements (XMCD & XRMR) have shown that the polarization is primarily in the first monolayer of U.

Mössbauer with ^{57}Fe shows the Fe near the U to be amorphous and non-magnetic

Wilhelm *et al.*, PRB 76, 024425 (2007)
Brown *et al.*, PRB 77, 014427 (2008)

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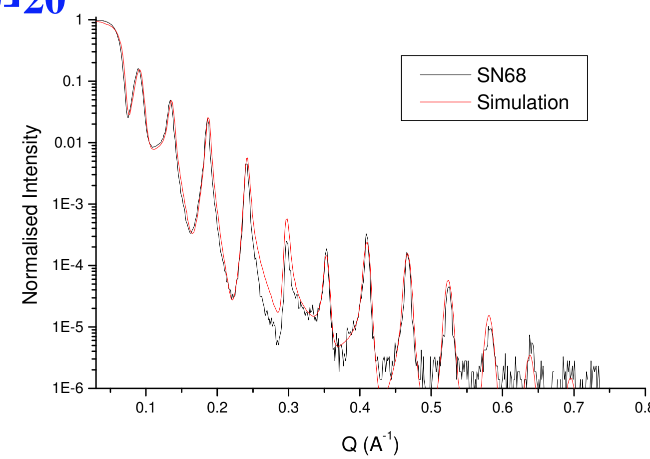
U/Gd multilayers

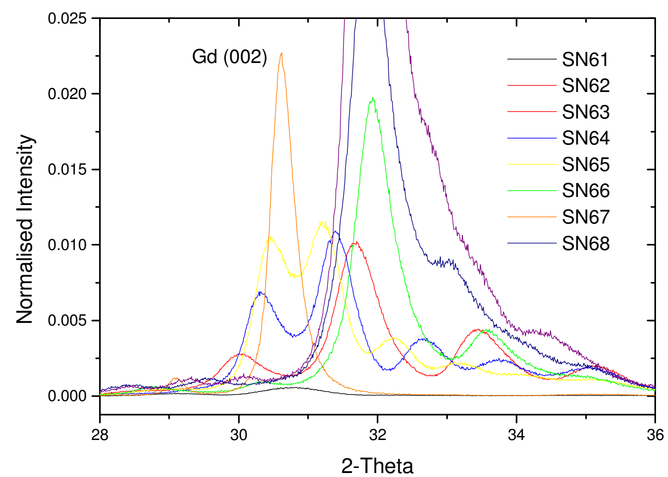
$[U_{50}/Gd_{50}]_{20}$

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.



Shows excellent crystallinity in Gd layers (lighter shade)

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.



Characteristics of U/Gd multilayers

Growth **good**. **Gd** shows crystallinity and preferred orientation (0001) growth, as expected. **U** shows partial crystallinity in a ***hcp*** structure. Roughness depends on thickness of Gd layer.

Magnetic characterization:

Gd moments are reduced strongly from 7 μ_B. We are still trying to understand this, but it is probably due to large grain growth and roughness at the interfaces due to **faceting**.

U **5*f*** polarization is small, but it is oscillatory in nature.

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U/Gd multilayers

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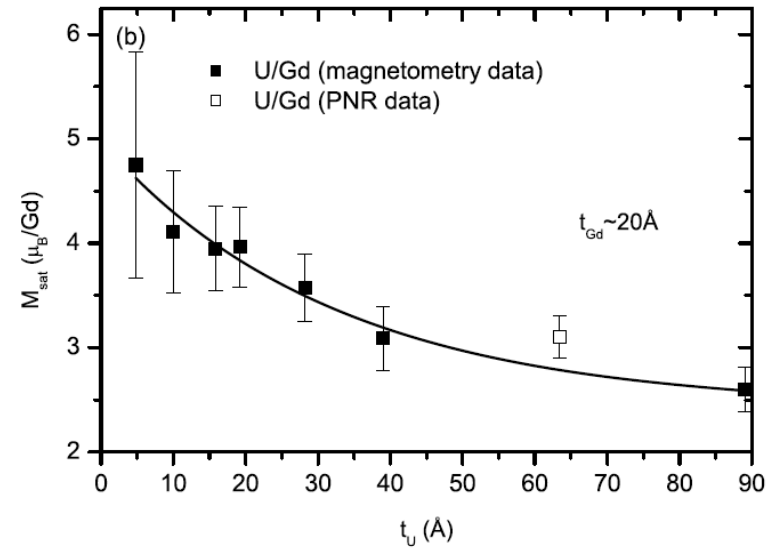
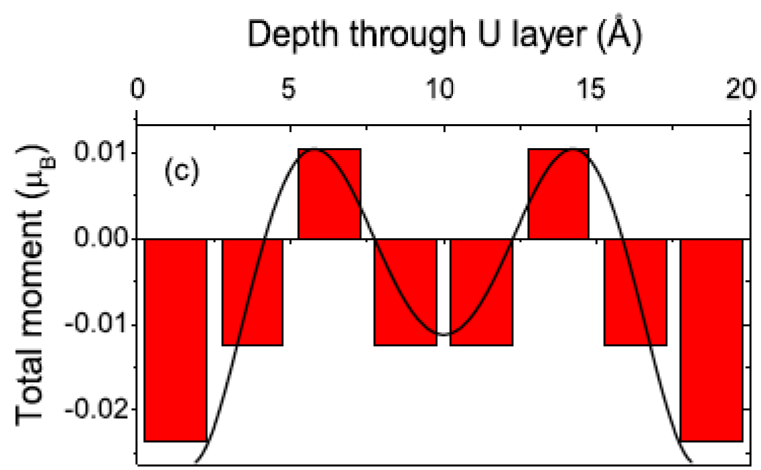
Interesting features are:

1: excellent multilayers with sharp interfaces, roughness depends on t_{Gd}

2: The large reduction of the Gd moment, which appears to depend on U thickness, t_U.

3: The small polarization, which is oscillatory in nature (20 times smaller than in U/Fe)





Springell *et al.*, JPCM <u>20</u> 215229 & 215230 (2008)

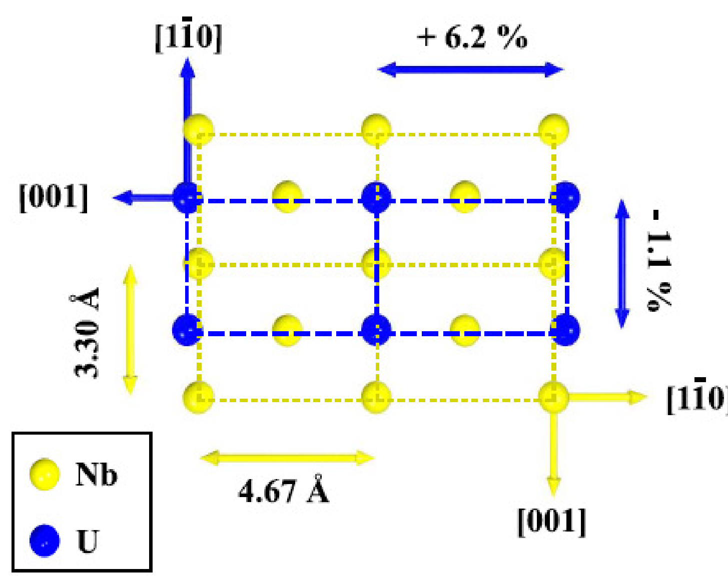
itu

Epitaxial layers of uranium

Growth of α–U on Nb buffers on sapphire sing-crystal substrates.

α–U grows with propagation axis [110]

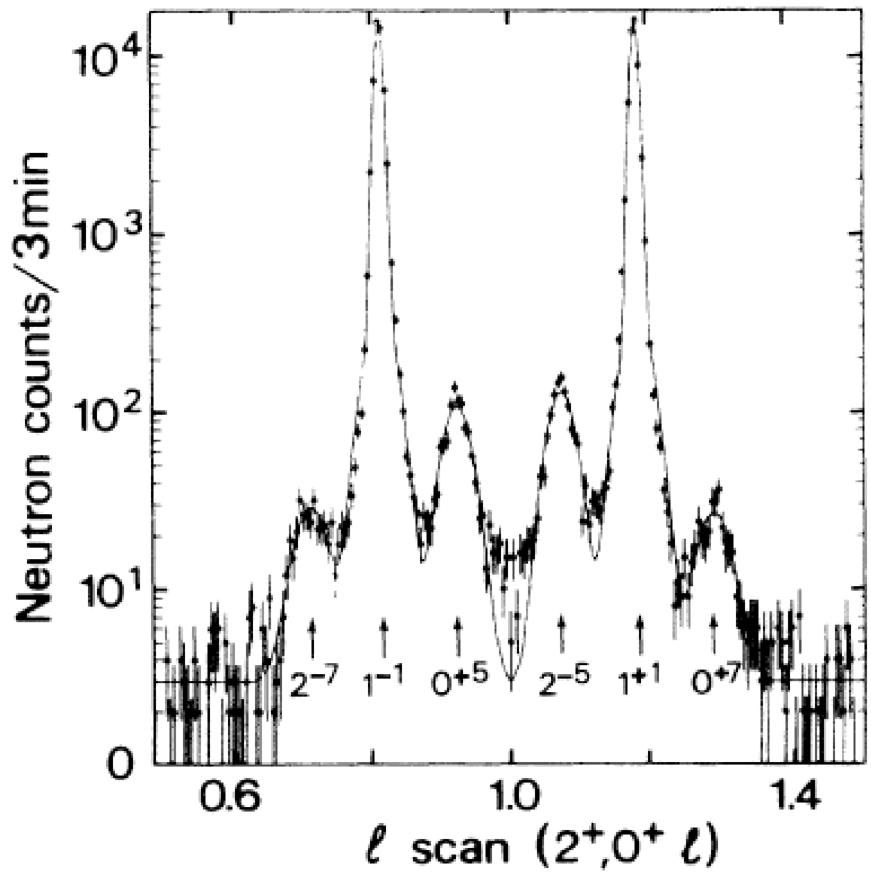
Good mosaic width. Very thin layers (< ~ 100 Å) show homo-epitaxial growth, i.e. they are pinned to the underlying Nb buffer.



Details of CDW

T = 15 K, D10, ILL

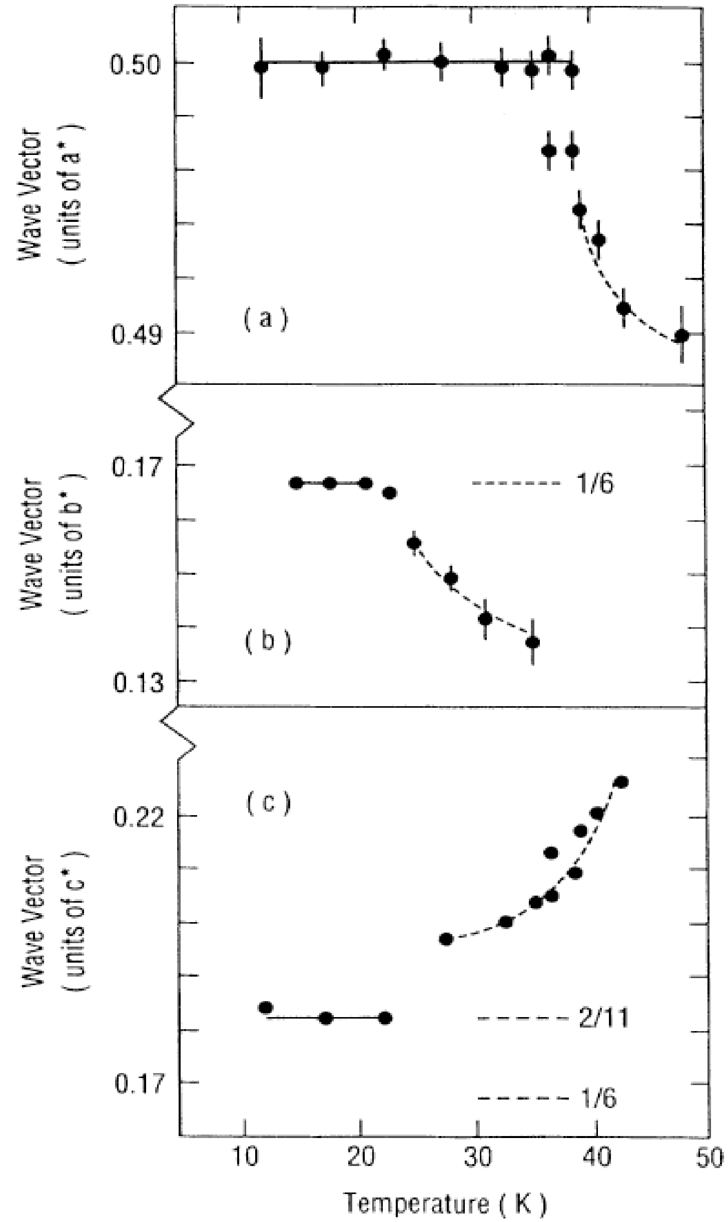
- **At the lowest T's the form of the CDW is governed to a large extent by 'strain' terms in the free energy.**
- **In an attempt to minimize the strain the displacements attempt to be 'square' - resulting in odd harmonics up to the 9th-order.**
- **Note 1st-order < 1% of structural peaks**



J. C. Marmeggi *et al.*, PRB 42 9365 (1990)
G. Grübel *et al.*, PRB 43 8803 (1991)

Structural details of CDW

- The details of the structural distortions in α–U have been characterized by a series of neutron and synchrotron x-ray experiments at ORNL, ILL, and NSLS
- Here we show the wave vector *q* (1/repeat distance) for each of the 3-dimensional components
- The most important motion (of ~ 0.04 Å) is that along the *a*–direction



G. H. Lander, E. S. Fisher and S. D. Bader, Adv. Physics 43 1-110 (1994)

Production of epitaxial films of U

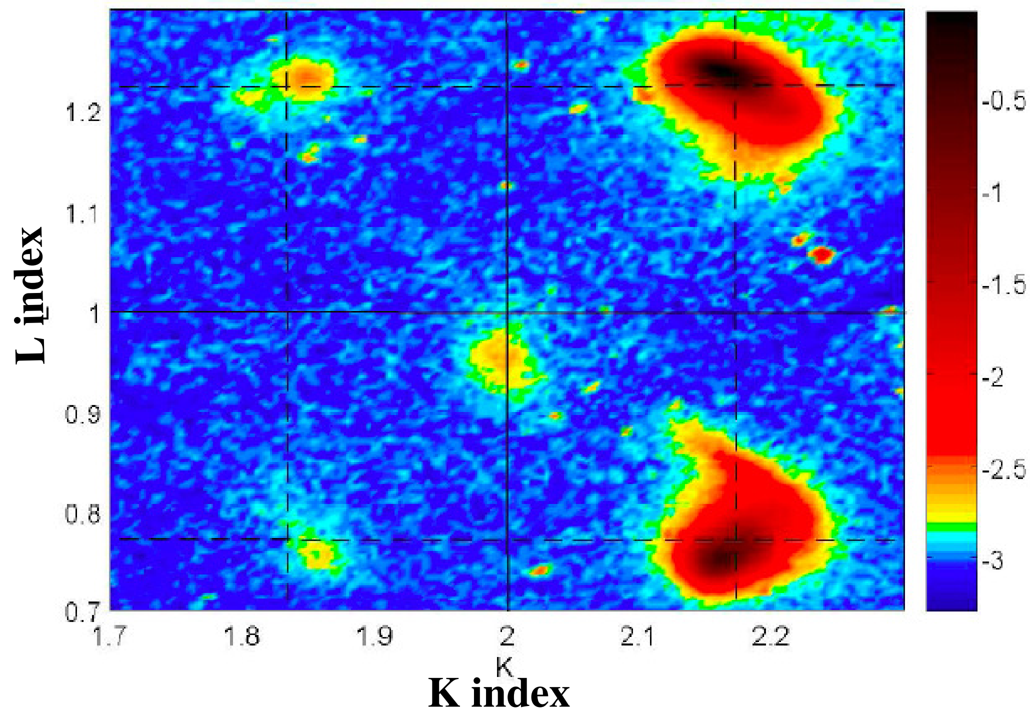
Dedicated sputtering apparatus at Clarendon Laboratory, Oxford

Roger Ward *et al.*

This has allowed multilayers of uranium to be fabricated and also *epitaxial films* of α-U to be produced using sapphire substrates and a buffer of *bcc*–Nb.

Observation of CDW in a 5000 Å film of α-U

View of reciprocal space at the position (2.5 K L)



R. Springell *et al.* PRB (in press)

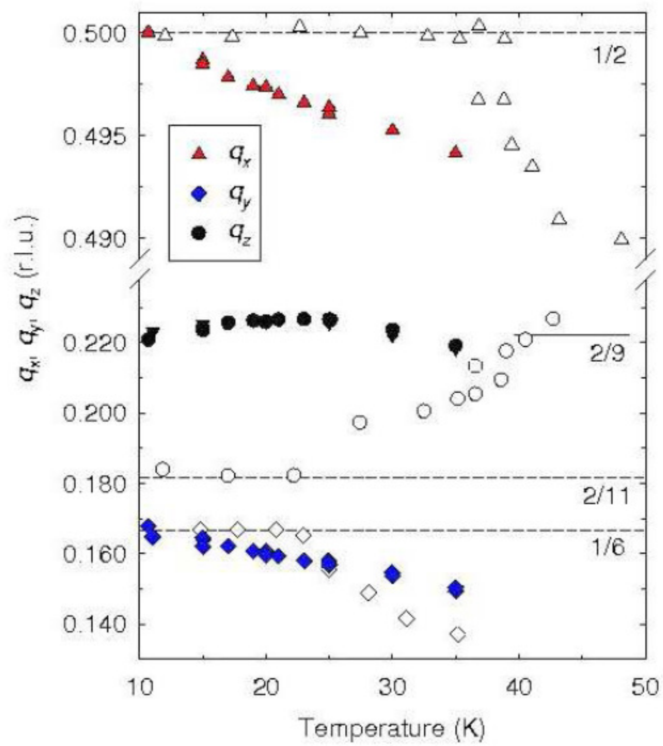
Results for CDW components

In general CDW of the 5000 Å film resembles that of the bulk, but there are some important differences.

(1) No lock-in transitions in film which suggests that strain is not an important factor in the films

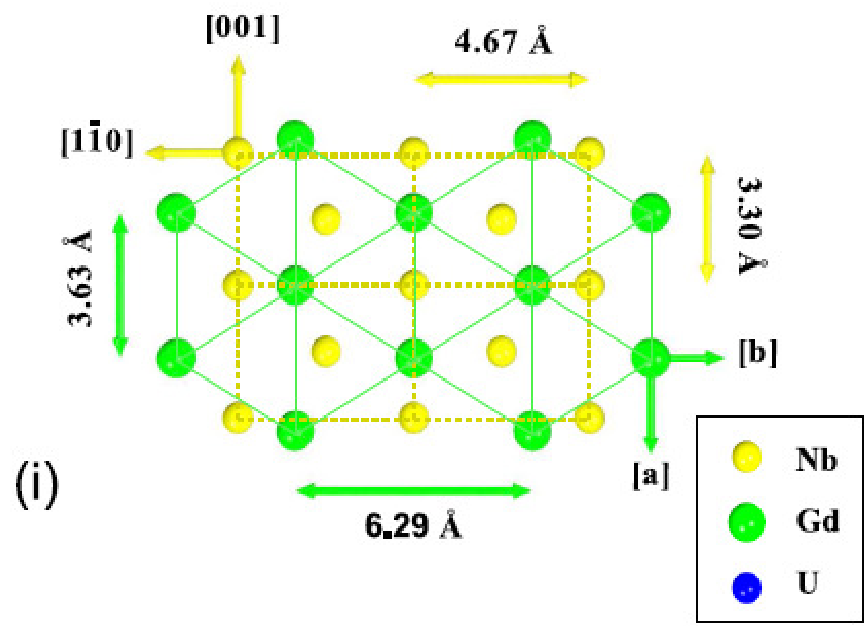
(2) Largest change (~ 20%) in q_z

(3) T_0 is reduced



Searching for *hcp*-U

Recall that *hcp*–U was found, by accident, in the U/Gd multilayers



It is well known that the *hcp* rare-earths can be grown epitaxially on Nb buffers.

Shown is *hcp* Gd on Nb.

hcp–U

Surprisingly, we find *two* orientational domains 30° apart.

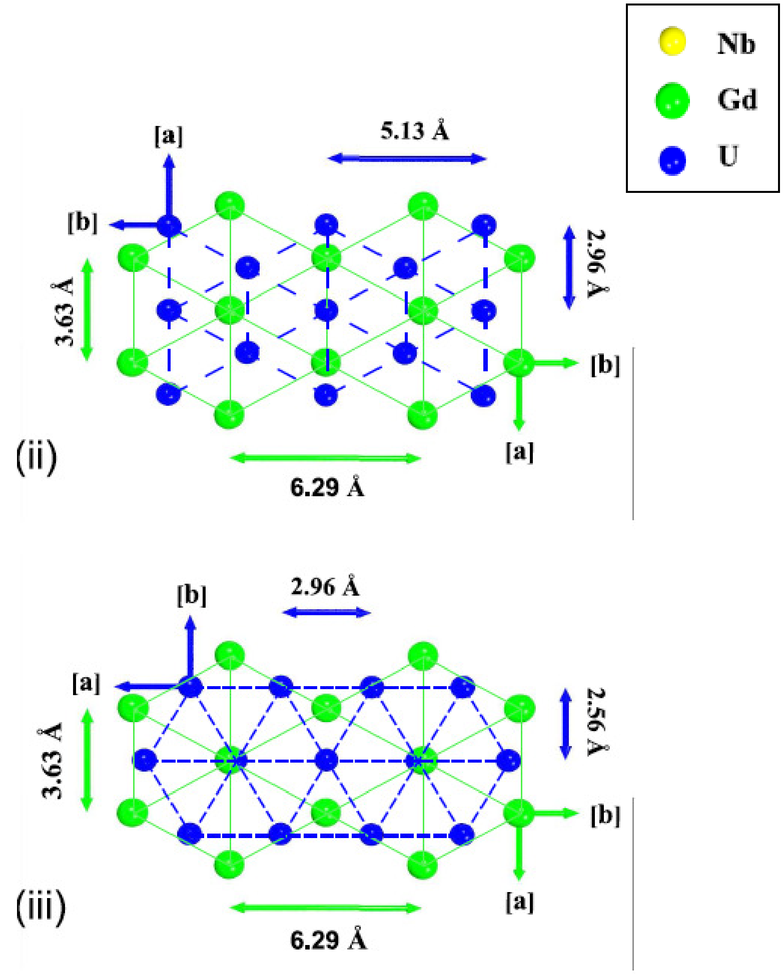
The figure shows the presumed relations with the Gd buffer.

Gd: a = 3.64 Å, c = 5.78 Å; c/a = 1.59

U: a = 2.96(2) Å, c = 5.63 Å; c/a = 1.90

Atomic vol: 21.3 Å^3/U; ideal c/a = 1.63

Calculations (University of Uppsala) have reproduced this value of c/a and suggested that *hcp*–U might be magnetic at low-temperature.



Joint Research Centre

Neutron & X-ray scattering with the facilities in Grenoble, France

- Neutrons at the ILL
- Focus on magnetism, neutrons couple to electron spin
- X-rays at the ESRF
- Structures at high pressure
- Resonant scattering effects

Surprises at the end of the periodic table

The elements slowly yield their secrets. Basic understanding in terms of itinerant to localized as function of filling of 5*f* shell

Compounds still very hard to understand. Case of superconductivity in Pu 115's is an example of the great challenges remaining, but there are many other fascinating materials and puzzles still to be resolved!

Thanks for your attention

Superconductivity in actinides

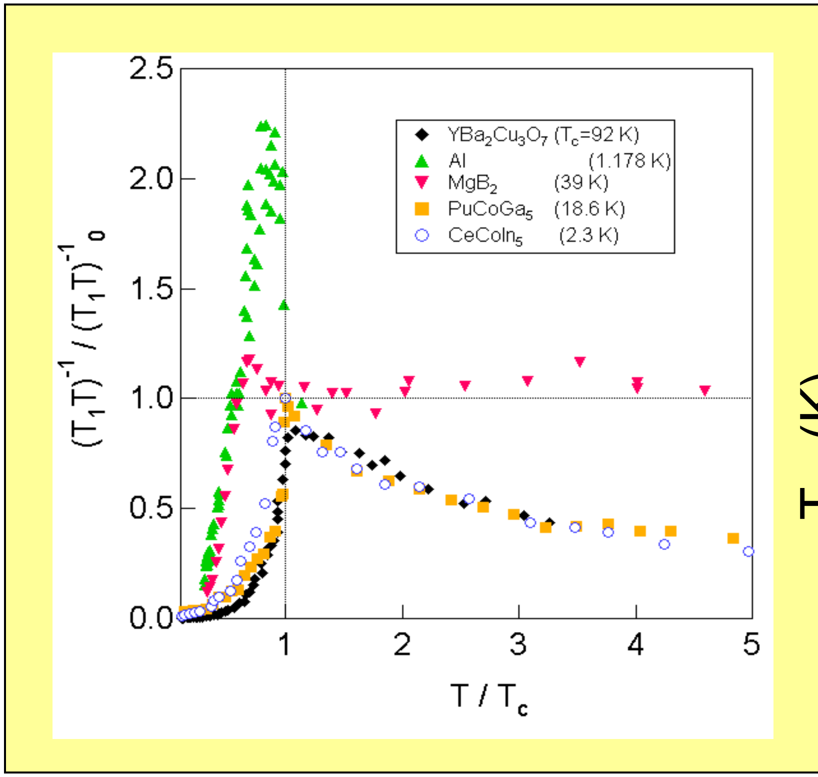
- **We have seen that U and Am are s/c at the 1-2 K level**
- **Other U heavy-fermion compounds, e.g. UBe_{13}, UPt_3 (discovered before high T_c in the 1980s) and UPd_2Al_3 (with T_c = 2.0 K) are classed as *unconventional* superconductors, i.e. they do not appear to have the s/c mediated by the BCS phonon mechanism.**

So we were *not* prepared for the discovery in 2002 of superconductivity in a Pu compound at the astonishing temperature of 18 K!

J. Sarrao *et al*., Nature 420, 297 (2002)

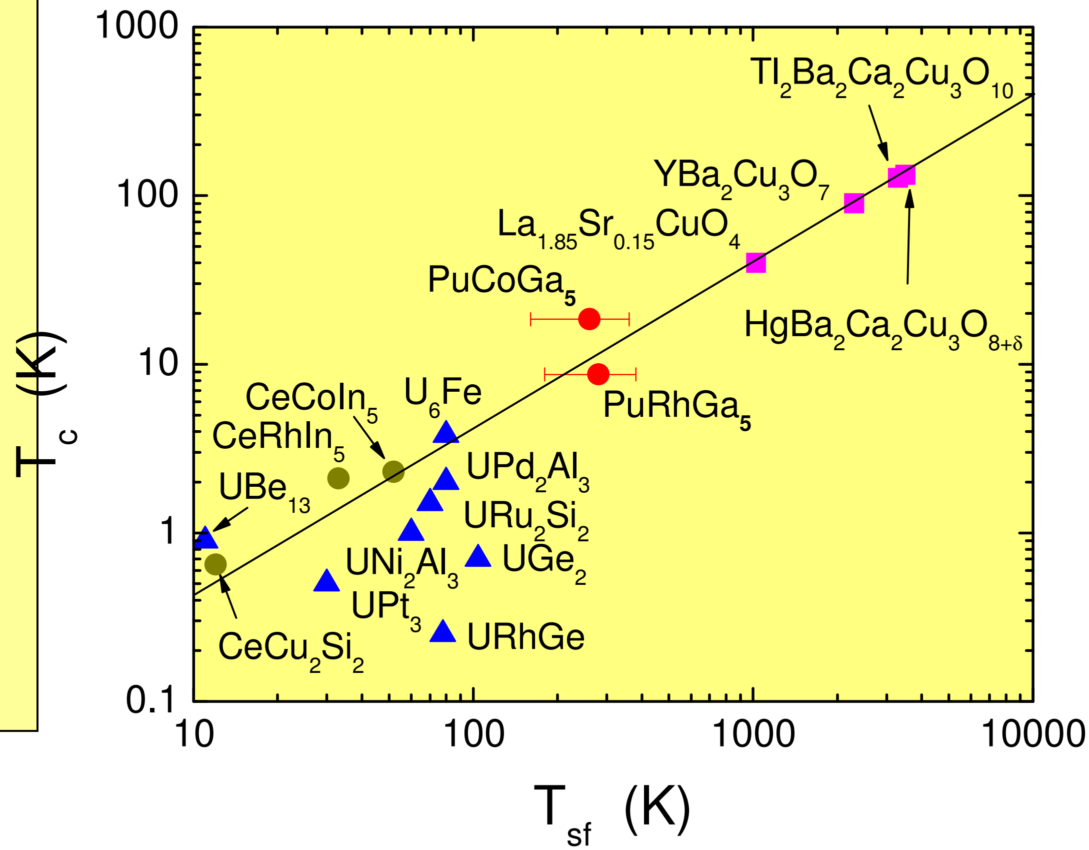
From Joe Thompson, LANL

Universal spin fluctuation tuning?



N. J. Curro et al., Nature **434**, 622 (2005).

after T. Moriya and K. Ueda, Rep. Prog. Phys. **66**, 1299 (2003)



Need Independent measures of T_{sf}?

October 08

Acknowledgments for 115 compounds

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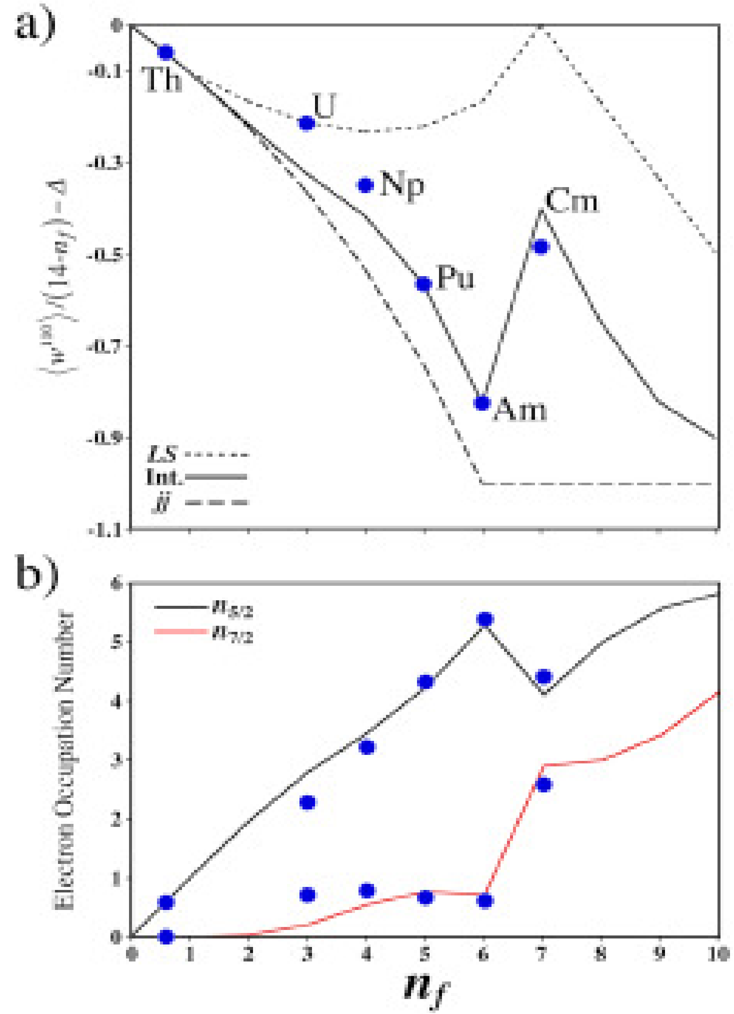
•**JAEA**: (Tokai) Yoshinora Haga, Naoto Metoki, Russ Walstedt, Hironori Sakai, Hiroshi Yasuoka

•**Uppsala**: Peter Oppeneer (theory)

Electron energy loss spectroscopy; measuring at $N_{4,5}$ edges ($4d \rightarrow 5f$ transitions)

(a) Related to branching ratio

(b) Population j=5/2 & 7/2



Kevin Moore (LLNL) *et al*: PRB submitted